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(21) International Application Number: PCT/US96/13352 (22) International Filing Date: 15 August 1996 (15.08.96) (30) Priority Data: 08/519,836 25 August 1995 (25.08.95) US (71) Applicants: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). (72) Inventors: BURKE, Patrick, Michael; 4613 Talley Hill Lane, Wilmington, DE 19803-4815 (US). GELLING, Onko, Jan; Maaslaan 62, NL-6163 KL Geleen (NL). OEVERING, Henk; Burg Eussenstraat 46, NL-6181 BR Stein (NL). TOTH, Imre; Henri Hermanslaan 48, NL-6162 GH Geleen (NL). (74) Agent: DEITCH, Gerald, E.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: CA, CN, JP, KR, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: HYDROFORMYLATION PROCESS (57) Abstract A hydroformylation process for the production of linear aldehydes of an olefin, with hydrogen and carbon monoxide in a solvent containing a catalyst having a platinum component, a bidentate diaryl phosphine component where the bridging group is ferrocenyl, and an acid promotor component.		

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TITLE

Hydroformylation Process

5 Field of the Invention

 This invention relates to the hydroformylation of olefins to form the corresponding linear aldehyde.

10 Background of the Invention

 Botteghi et al. in Journal of Organometallic Chemistry 417 (1991) C41-C45 in an article titled "Hydroformylation of olefins catalyzed by alkene complexes of platinum(0)" disclose hydroformylation using a bidentate phosphino compound, a platinum catalyst, and an acid promoter in an organic solvent. This article notes: "... , internal double bonds are rather unreactive as shown by the hydroformylation of cyclohexene...."

20 U.S. Patent 4,528,278 to Hsu describes a hydroformylation catalyst comprising a platinum compound, a ferrocene derived ligand and a Group IV metal halide.

 An object of the present invention is to provide a process for the hydroformylation of olefins to form linear products.

Summary of the Invention

 The present invention is a process for the preparation of linear aldehyde which comprises contacting an olefin, hydrogen and carbon monoxide in a solvent containing a dissolved catalyst comprising (a) a platinum compound free of anionic halide, (b) a bidentate diaryl phosphine ligand having the formula $Ar_2P-Q-Ar_2P$ where Q is a ferrocenyl group and each Ar group has 6 to 15 carbon atoms, (c) an acid promoter selected from (1) sulfonic acids having a pKa in water of less than -3, (2) tetrafluoroboric acid, (3) a

fluorine substituted aryl boronic acid of the formula:
[HZ]+[B(Ph)₄]- where Z is an oxygen containing Lewis
base and Ph is a fluorine or trifluoromethyl
substituted phenyl group, and (4) hexafluorophosphoric
5 acid and where the ratio (c) to (a) is in the range
0.5/1 to 3/1, and where the ratio of (b) to (a) is in
the range 1.0/1 to 1.5/1.

Preferably, the olefin contains 4 to 10
carbon atoms.

10 The process may effectively be carried out at
a temperature in the range of 80 to 120°C and the
carbon monoxide partial pressure and hydrogen partial
pressure is in the range of 200 to 2000 pounds per
square inch.

15 The present invention is also a composition
comprising solvent containing a dissolved catalyst
comprising, (a) a platinum compound free of anionic
halide, (b) a bidentate diaryl phosphine ligand having
the formula Ar₂P-Q-PAr₂ where Q is a ferrocenyl group
20 and each Ar group has 6 to 15 carbon atoms, and (c) an
acid promoter selected from (1) sulfonic acids having a
pKa in water of less than -3, (2) tetrafluoroboric
acid, (3) a fluorine substituted aryl boronic acid and
hexafluorophosphoric acid; and where the ratio (c) to
25 (a) is in the range 0.5/1 to 3/1, and where the ratio
of (b) to (a) is in the range 1.0/1 to 1.5/1.

Suitable solvents include acetonitrile,
adiponitrile, methylglutaronitrile, dimethyladipate,
valerolactone, methylisobutylketone, methylene
30 chloride, sulfones, such as sulfolane, mixtures of one
of the above nitriles and toluene, and homogenous
mixtures of the above nitriles and water. When the
process of the present invention is operated in a
continuous manner, the product will be removed from the
35 solvent and the solvent recycled, and gradually the
composition of the solvent will change as more and more
by-products of the reaction remain in the recycled
solvent.

One of the preferred bidentate diaryl phosphine ligand having the formula $\text{Ar}_2\text{P-Q-PAr}_2$ is 1,1'-bis(diphenylphosphino)ferrocene.

One of the preferred acid promoters is
5 trifluoromethanesulfonic acid.

Detailed Description

Suitable olefins for hydroformylation into linear aldehydes include: (1) pentenoic acid esters
10 such as 2- and 3-pentenoic acid esters where the non-pentenoic acid portion is from a hydrocarbon alcohol. The hydrocarbon alcohol may be saturated or unsaturated, aliphatic or aromatic; but usually will have from 1 to 8 carbon atoms, (2) 2 and 3-
15 pentenenitriles, (3) 2-, and 3-pentenoic acids, and (4) hydrocarbon olefins such as 4-octene, 2-butene, and 2-hexene.

The organic solvent for use in the process should dissolve the platinum catalyst compound, the
20 compound to be hydroformylated, the bidentate diarylphosphine ligand, the acid promoter, and the product. Stated another way, the solvent should provide a homogenous reaction mixture. Suitable solvents include acetonitrile, adiponitrile,
25 methylglutaronitrile, dimethyladipate, caprolactone, dichloromethane, 2-butanone, propylenecarbonate, valerolactone, methylisobutylketone, methylene chloride, mixtures of one of the above nitriles and toluene, homogenous mixtures of the above nitriles and
30 water, and sulfones, such as sulfolane. When the process of the present invention is operated in a continuous manner, the product will be removed from the solvent and the solvent recycled, and gradually the composition of the solvent will change as more and more
35 by-products of the reaction remain in the recycled solvent.

The platinum component of the catalyst must be free of anionic halide, but may contain covalent

halide, e.g., fluorinated beta-diketonate.

Platinum(II) beta-diketones, platinum (II) carboxylates, and platinum complexes such as Pt(cyclooctadiene)₂ may be the platinum catalyst component.

5 The acid promoter component of the catalyst is selected from (1) sulfonic acids having a pKa in water of less than -3, (2) tetrafluoroboric acid, (3) a fluorine substituted aryl boronic acid and
10 hexafluorophosphoric acid. Trifluoromethanesulfonic acid is one of the preferred acid. Some acids of the formula: HB(Ar)₄, specifically [(3,5-(CF₃)₂C₆H₃)₄B]-[H(OET)₂]⁺ are also quite effective. (This is the etherate solvate of the free acid). See: Brookhart, M.; Grant, B.; and Volpe, Jr., A. F. Organometallics,
15 1992, 11, 3920.

 The bidentate diaryl phosphine ligand having the formula Ar₂P-Q-PAr₂ where Q a ferrocenyl group and each of the Ar groups contain 6 to 15 carbon atoms include such compounds as:

20 1,1-Bis(diphenylphosphino)ferrocene;
1,1'Bis(di-m-fluorophenylphosphino)ferrocene;
1,1'Bis(di-p-methylphenylphosphino)ferrocene;
1,1'Bis(diphenylphosphino)3,3'-(trimethylsilyl)ferrocene;
25 1,1'Bis(di-p-trifluoromethylphenylphosphino)ferrocene;
and, 1,1'Bis(di-3,5(bis(trifluoromethyl)phenylphosphino)ferrocene.

 The present invention is a process for the preparation of linear aldehyde which comprises
30 contacting an olefin, hydrogen and carbon monoxide in a solvent containing a dissolved catalyst comprising (a) a platinum compound free of anionic halide, (b) a bidentate diaryl phosphine ligand having the formula Ar₂P-Q-Ar₂P where Q is a ferrocenyl group and each Ar
35 group has 6 to 15 carbon atoms, (c) an acid promoter selected from (1) sulfonic acids having a pKa in water of less than -3, (2) tetrafluoroboric acid, (3) a fluorine substituted aryl boronic acid and

hexafluorophosphoric acid and where the ratio (c) to (a) is in the range 0.5/1 to 3/1, and where the ratio of (b) to (a) is in the range 1.0/1 to 1.5/1.

In order to be most effective the ratio acid promoter to platinum compound should be is in the range 0.5/1 to 3/1, and the ratio of bidentate diaryl phosphine ligand to platinum compound should be in the range 1.0/1 to 1.5/1. The platinum component should be in the reaction mixture to the extent of 500 to 5000 parts per million parts of the reaction mixture. The usual amount of platinum component will be about 2000 parts per million parts of reaction mixture.

The process can be operated at a temperature range of 70 to 120°C, preferably at a temperature in the range of 90 - 110°C.

EXAMPLES

Example 1

Hydroformylation of Hexene-2 with Pt(AcAc)₂ + DPPF + Trifluoromethanesulfonic Acid, also called Triflic Acid in 4/1 Toluene-acetonitrile Solvent

A 25 ml glass lined shaker tube was charged with 5 ml of a solution containing 0.42 g (5 mmole) 2-hexene, 19.6 mg (0.05 mmole) platinum acetylacetonate (Pt(AcAc)₂), 6.0 mg (0.04 mmoles) triflic acid and 50 mg tetradecane (internal GC standard) in a solvent consisting of 4 parts by weight of toluene to 1 part by weight of acetonitrile. To this solution was added 35 mg (0.0625 mmole) of 1,1'-Bis(diphenylphosphino)ferrocene (DPPF).

The shaker tube was freed from air by purging first with 100 psi nitrogen (twice) and then with 1:1 CO/H₂ (twice). The tube was then pressurized to 700 psi CO/H₂ and heated 100°C over 20 minutes. The pressure was then adjusted with 1:1 CO/H₂ to 1000 psi at 100°C. The temperature was maintained at 100°C with shaker agitation for 6 hours. The heat was shut off,

and the shaker tube was allowed to cool to 25-35°C. The excess CO/H₂ was vented, and the product was analyzed on a capillary GC column. The results are summarized in Table 1.

5		<u>Mole %</u>	<u>Selectivities</u>
	Recovered Mixed Hexenes	50.6	
	<u>Products</u>		
	Heptanal	20.7	88.5
10	2-Methylhexanal	1.7	7.2
	2-Methylpentanal	0.3	1.3
	Hexane	0.7	2.3
	Linearity	91.3%	

15

The results demonstrate the very high selectivity to the linear product, from an internal olefin using the above platinum catalyst. Thus, the selectivity to the desired product, heptanal is >88% at 20 23% conversion to aldehydes and the linearity (100* Heptanal/(all aldehydes)) is 91.3%.

Note: Selectivity to a product is defined here as:
 100*(Moles Product)/Sum of (moles of all
 25 products detected by the GC analysis).

In the following examples, the products were analyzed in the same way but the results are expressed in summary form as combined conversion of the olefin and its double bond isomers ("Conv"), selectivity to
 30 linear aldehyde ("Sel"), and linearity ("Lin").

Examples 2-7

Hydroformylation of Hexene-1 and Hexene-2 with DPPF Ligand and Various Acid Promoters

35 The experiment in Example 1 was repeated except that the acid promoter and the hexene isomer were varied and where indicated, the solvent also

contained water (50 or 100 equivalents per Pt). The results are shown in Table 1.

TABLE 1

5

<u>Ex</u>	<u>Olefin</u>	<u>Acid</u>	<u>Water Eq/Pt</u>	<u>Conv</u>	<u>Sel to Hp-al</u>	<u>Lin</u>
2	Hexene-2	HB F_4	50	33.8	90.5	91.5
3	Hexene-2	Triflic	50	29.0	85.1	86.6
10 4	Hexene-2	HP F_6	50	28.6	88.7	89.8
5	Hexene-1	HB F_4	50	75.5	93.5	94.8
6	Hexene-1	HP F_6	50	67.4	93.4	94.8
7	Hexene-1	PFOSA (5/Pt)	0	58.9	82.2	85.2

15

PFOSA = Perfluoro-octanesulfonic acid

The above results demonstrate that high yields of linear aldehyde can be obtained with different strong acid promoters and with both internal and terminal olefins.

Examples 8-10 M4P Hydroformylation

Hydroformylation of Methyl-4-Pentenoate (M4P) with Pt(AcAc) $_2$ + DPPF + Acid

The experiment in Example 1 was repeated except that the Hexene-2 was replaced with an equivalent amount of methyl-4-pentenoate (M4P). The results are shown in Table 2.

30

TABLE 2

<u>Ex</u>	<u>Olefin</u>	<u>Acid</u>	<u>Water</u>	<u>Conv</u>	<u>Sel to M5FV</u>	<u>Lin</u>
35 8	M4P	HB F_4	50	89.3	92.5	93.8
9	M4P	Triflic	50	85.9	89.7	93.1
10	M4P	HP F_6	50	88.8	92.4	93.3

The above results demonstrate that high yields can be obtained with this catalyst system with a terminal functional olefin.

5 **Example 11**

M3P Hydroformylation with Pt(AcAc)₂ + Triflic Acid in Acetonitrile Solvent

A 25 ml glass lined shaker tube was charged with 5 ml of an acetonitrile solution containing 3.42 g
10 (30 mmole) methyl-3-pentenoate, 19.6 mg (0.05 mmole) Platinum acetylacetonate (Pt(AcAc)₂) and 50 mg tetradecane (internal GC standard). To this solution was added 28 mg (0.05 mmole) of 1,1'-
15 Bis(diphenylphosphino)ferrocene and 6 mg (0.04 mmoles) of triflic acid. The solution was allowed to stand in a nitrogen atmosphere for 18 hours before commencing the hydroformylation.

The shaker tube was freed from air by filling first with 100 psi nitrogen (twice) and then with 1:1
20 CO/H₂ (twice). The tube was then pressurized to 700 psi CO/H₂ and heated 100°C over 20 minutes. The pressure was then adjusted with 1:1 CO/H₂ to 1000 psi at 100°C. The temperature was maintained at 100°C with shaker agitation for 6 hours. The heat was shut off,
25 and the shaker tube was allowed to cool to 25-35°C. The excess CO/H₂ was vented, and the product was analyzed for methyl esters and formylvalerates on a capillary GC column. The results are summarized in Table 3.

30

Examples 12-17

M3P Hydroformylation with Pt(AcAc)₂ + Triflic Acid + DPPF or Various Substituted DPPF Ligands in Acetonitrile Solvent

35 The experiment in Example 11 was repeated, except that the ligand was varied to include 1,1'-Bis(diphenylphosphino)ferrocenes substituted on both the phenyl rings and the ferrocenyl moiety. The ratio

of ligand to Pt and of triflic acid to Pt and the temperature were also varied. The results are shown in Table 3.

5

TABLE 3

	<u>Ex</u>	<u>Ligand</u>	<u>Lig/</u> <u>Pt</u>	<u>Trif/</u> <u>Pt</u>	<u>Temp</u>	<u>Conv</u>	<u>Sel to</u> <u>M5FV</u>	<u>Lin</u>	<u>Aldol</u>
	11	DPPF	1.00	0.8	100	69.1	81.1	91.9	7.1
10	12	Ligand A	1.0	0.8	100	64.4	65.9	90.7	19.5
	13	Ligand B	1.0	0.8	100	24.8	64.5	81.2	2.4
	14	Ligand C	1.0	0.8	100	50.2	75.3	89.2	7.8
	15	DPPF	0.75	1.2	105	31.4	59.1	77.9	13.2
	16	DPPF	1.5	1.0	115	53.3	79.3	92.2	1.5
15	17	DPPF	1.5	0.7	95	27.7	87.3	91.4	0.0

DPPF = 1,1'-Bis(diphenylphosphino) ferrocene

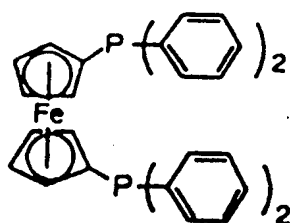
Ligand A = 1,1'-Bis(di-m-fluorophenylphosphino) ferrocene

20 Ligand B = 1,1'-Bis(di-p-tolylphosphino) ferrocene

Ligand C = 1,1'-Bis(diphenylphosphino)-3,3'-bis(trimethylsilyl) ferrocene

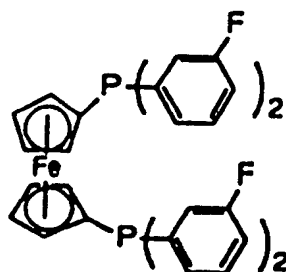
These ligands have the following structural formulas:

5



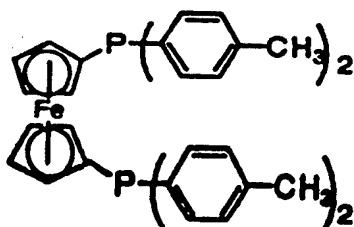
DPFF

10



Ligand A

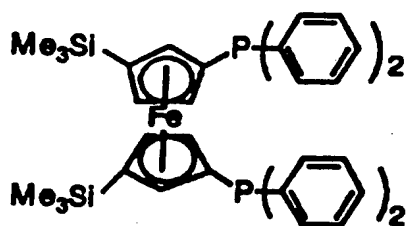
15



Ligand B

20

25



Ligand C

30

The results show that an internal functional olefin (M3P) can be hydroformylated with high selectivity to the linear aldehyde with an acid promoted Pt catalyst and DPFF or its substituted derivatives.

Examples 18-21

1-Hexene Hydroformylation in Sulfolane

Solvent

The experiment in Example 1 was repeated
 5 except that the olefin was Hexene-1, the solvent was
 sulfolane and an external GC standard was used for the
 analysis. In some examples, water or acetonitrile was
 used as a co-promoter for the Pt catalyst. The results
 are shown in Table 4.

10

TABLE 4

	<u>Ex</u>	<u>DPPF/ Pt</u>	<u>Trif/ Pt</u>	<u>Co-Pro moter</u>	<u>CP/Pt</u>	<u>Conv</u>	<u>Sel to M5FV</u>	<u>Lin</u>
15	18	1.25	0.8	None	--	90.3	86.1	86.6
	19	1.25	0.8	Water	50	88.6	87.4	88.0
	20	1.25	0.8	CH ₃ CN	50	93.1	91.3	91.8
	21	1.25	0.8	CH ₃ CN	400	92.1	92.1	92.6

20 CP/Pt = Co-promoter to platinum mole ratio

The results show that high rates and
 selectivities can be obtained in sulfolane solvent and
 that rates and selectivities can be further enhanced in
 25 the presence of water or acetonitrile.

Examples 22-27

3-Pentenoic Acid Hydroformylation

The experiment in Example 1 was repeated
 30 except that the methyl-3-pentenoate was replaced with
 an equivalent amount of 3-pentenoic acid, the platinum
 source was Pt(AcAc)₂ and the water and acid promoter
 were varied. The products were analyzed directly as
 the formyl acids on a capillary GC column. The results
 35 are summarized in Table 5.

TABLE 5

	<u>Ex</u>	<u>Acid</u>	<u>Acid/ Pt</u>	<u>Ligand</u>	<u>Lig/ Pt</u>	<u>H₂O/ Pt</u>	<u>Conv</u>	<u>Sel to 5FVA</u>	<u>Lin</u>
5	22	Triflic	0.8	DPPF	1.25	50	83.3	85.1	91.0
	23	Triflic	1.0	DPPF	1.25	50	71.4	65.7	83.2
	24	Triflic	1.0	DPPF	1.25	0	66.3	49.5	72.7
	25	HBF ₄ (54% aq)	1.0	DPPF	1.25	50	69.1	81.9	90.7
10	26	HPF ₆ (60% aq)	1.0	DPPF	1.25	50	80.3	83.8	90.8
	27	PFOSA	5.0	DPPF	1.25	50	90.2	83.6	90.1

The results show that very high yield of 5-formylvaleric acid can be obtained from 3-pentenoic acid with the acid promoted platinum catalysts of this invention. Further, it can be seen that yields are improved by adding a small quantity of water (e.g., about 50 equivalents of water per equivalent of Pt).

20

Examples 28 3PN Hydroformylation

The experiment in Example 1 was repeated except that the M3P was replaced with 3-pentenitrile (3PN), the mole ratio of water to Pt was 20. The products (formylvaleronitriles and valeronitrile) were analyzed directly by capillary GC. The results are summarized in Table 6.

25

TABLE 6

30

	<u>Ex</u>	<u>Ligand</u>	<u>Lig/ Pt</u>	<u>Conv</u>	<u>Sel to 5FVN*</u>	<u>Lin</u>	<u>Acctg</u>
	28	DPPF	1.25	9.3	76.8	92.2	99

The results show that 3PN gives primarily linear product with this catalyst system.

35

*5FVN = 5-formylvaleronitrile

What is Claimed is:

1. A process for the preparation of linear aldehyde which comprises contacting an olefin, hydrogen and carbon monoxide in a solvent containing a dissolved catalyst comprising (a) a platinum compound free of anionic halide, (b) a bidentate diaryl phosphine ligand having the formula $\text{Ar}_2\text{P-Q-Ar}_2\text{P}$ where Q is a ferrocenyl group and each Ar group has 6 to 15 carbon atoms, (c) an acid promoter selected from (1) sulfonic acids having a pKa in water of less than -3, (2) tetrafluoroboric acid, (3) a fluorine substituted aryl boronic acid of the formula: $[\text{HZ}]+[\text{B}(\text{Ph})_4]^-$ where Z is an oxygen containing Lewis base and Ph is a fluorine or trifluoromethyl substituted phenyl group, and (4) hexafluorophosphoric acid and where the ratio (c) to (a) is in the range 0.5/1 to 3/1, and where the ratio of (b) to (a) is in the range 1.0/1 to 1.5/1.

2. The process of claim 1 in which the olefin contains 4 to 10 carbon atoms.

3. The process of claim 1 in which the olefin is a methyl pentenoate and the linear aldehyde is methyl-5-formylvalerate.

4. The process of claim 1 in which the solvent is selected from the group consisting of acetonitrile, adiponitrile, methylglutaronitrile, dimethyladipate, valerolactone, methylisobutylketone, methylene chloride, mixtures of one of the above nitriles and toluene, and mixtures of the above nitriles and water.

5. The process of claim 1 in which the temperature is in the range of 80 to 120°C and the carbon monoxide partial pressure is in the range of 250 to 3000 pounds per square inch.

6. A composition comprising solvent containing a dissolved catalyst comprising (a) a platinum compound free of anionic halide, (b) a bidentate diaryl phosphine ligand having the formula $\text{Ar}_2\text{P-Q-PAr}_2$ where Q is a ferrocenyl group and each Ar

group has 6 to 15 carbon atoms, and (c) an acid promoter selected from (1) sulfonic acids having a pKa in water of less than -3, (2) tetrafluoroboric acid, (3) a fluorine substituted aryl boronic acid of the
5 formula: $[HZ] + [B(Ph)_4]^-$ where Z is an oxygen containing Lewis base and Ph is a fluorine or trifluoromethyl substituted phenyl group, and (4) hexafluorophosphoric acid; and where the ratio (c) to (a) is in the range 0.5/1 to 3/1, and where the ratio
10 of (b) to (a) is in the range 1.0/1 to 1.5/1.

7. The composition of claim 6 in which the solvent the selected from the group consisting of acetonitrile, adiponitrile, methylglutaronitrile, dimethyladipate, valerolactone, methylisobutylketone,
15 methylene chloride, mixtures of one of the above nitriles and toluene, and mixtures of the above nitriles and water.

INTERNATIONAL SEARCH REPORT

L ational Application No
PCT/US 96/13352

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C45/50 C07C67/347 C07C69/716 B01J31/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 220 767 A (SHELL INT RESEARCH) 6 May 1987 see the whole document ---	1-5
Y	EP 0 529 698 A (SHELL INT RESEARCH) 3 March 1993 see the whole document ---	1-5
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